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Process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas and system therefor

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ABSTRACT

This invention provides a process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas wherein a raw gas (1) containing carbon dioxide is fed to a decarbonation tower (2) where the raw gas (1) is brought into gas-liquid contact with a partially regenerated absorbing fluid (21) in a lower absorption section (3) so as to cause carbon dioxide to be partially absorbed thereinto, and then brought into gas-liquid contact with a regenerated absorbing fluid (22) in an upper absorption section (4) so as to cause carbon dioxide to be absorbed thereinto until a very low carbon dioxide concentration is reached; and high-pressure carbon dioxide is recovered from the resulting carbon dioxide-loaded absorbing fluid (20), as well as a system therefor.

This invention makes it possible to remove highly concentrated carbon dioxide from high-pressure natural gas and various synthesis gases with the aid of a carbon dioxide absorbing fluid until a very low carbon dioxide concentration is reached and, moreover, to recover high-pressure carbon dioxide from the absorbing fluid.

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INVENTION TITLE:

"PROCESS FOR THE REMOVAL
AND HIGH-PRESSURE RECOVERY
OF CARBON DIOXIDE FROM A
HIGH-PRESSURE RAW GAS AND
SYSTEM THEREFOR"

The following Statement is a full description of this invention including the best method of performing it known to me:

SPECIFICATION

TITLE OF THE INVENTION

Process for the Removal and High-Pressure Recovery of
Carbon Dioxide from a High-Pressure Raw Gas and System
Therefor

BACKGROUND OF THE INVENTION

1. Field of the invention

This invention relates to a process for treating a high-pressure raw gas selected from high-pressure natural gas and various synthesis gases with a carbon dioxide absorbing fluid, whereby highly concentrated carbon dioxide (CO₂) is fully removed from the raw gas to obtain a refined gas having a carbon dioxide concentration of 10 to 10,000 ppm and, moreover, for recovering high-pressure carbon dioxide from the absorbing fluid, as well as a system therefor.

2. Description of the related art

Usually, high-pressure natural gas may contain a considerable amount (e.g., 10 to 20%) of carbon dioxide. When such natural gas is converted to liquefied natural gas (hereinafter referred to as LNG), carbon dioxide forms dry ice as a result of cooling, and this solid material may cause problems such as obstruction of the system. Accordingly, its carbon dioxide concentration must be reduced to 50 ppm or less.

Moreover, in the case of ammonia-urea synthesis, a gaseous

mixture composed of hydrogen, carbon monoxide, carbon dioxide and the like is obtained by the partial oxidation or steam reforming of natural gas, naphtha or the like. This gaseous mixture is subjected to a CO shift reaction for converting carbon monoxide to carbon dioxide, and used as a raw material for ammonia synthesis after the separation of carbon dioxide. On the other hand, the separated carbon dioxide is pressurized to 100-200 atmospheres and reacted with ammonia to form urea. Accordingly, the carbon dioxide concentration of a raw material for ammonia synthesis must generally be reduced to the order of 500 ppm.

Furthermore, in the case of hydrogen gas for use in chemical syntheses, its carbon dioxide concentration must be reduced to a level ranging from several tens to several thousands of parts per million, depending on its application.

In order to use the separated carbon dioxide for the purpose of tertiary oil recovery (EOR), liquid carbon dioxide production or urea synthesis or store it in an underground aquifer as a countermeasure against global warming, it must be pressurized to a pressure ranging from several tens to several hundreds of atmospheres.

Consequently, it would be desirable to remove carbon dioxide from an inherently high-pressure raw gas until a very low carbon dioxide concentration is reached and recover the removed carbon dioxide in a high-pressure state. However, no

method useful for this purpose has been known in the prior art.

In the prior art, the following process has been employed to remove carbon dioxide until a very low carbon dioxide concentration (for example, of the order of 100 ppm) is reached. First of all, a gas is fed to the bottom of a decarbonation tower while a carbon dioxide absorbing fluid is fed to the top of the decarbonation tower. Thus, the gas is brought into gas-liquid contact with the absorbing fluid, so that carbon dioxide is absorbed thereinto and removed. Then, the absorbing fluid having carbon dioxide absorbed thereinto (hereinafter referred to as the loaded absorbing fluid) is introduced into a regeneration tower where carbon dioxide is liberated by steam stripping to obtain a regenerated absorbing fluid. This regenerated absorbing fluid is fed to the decarbonation tower.

Moreover, another example of the method for removing carbon dioxide from high-pressure natural gas and recovering the removed carbon dioxide in a high-pressure state is a process for the bulk removal of carbon dioxide.

However, the above-described conventional processes for the high removal and high-pressure recovery of carbon dioxide and systems therefor involve the following problems.

(1) In the above-described process using a carbon dioxide absorbing fluid, the carbon dioxide concentration of the

regenerated absorbing fluid can be reduced and, therefore, carbon dioxide can be removed until a very low carbon dioxide concentration is reached. However, since the absorbing fluid is regenerated by depressurization, it is difficult to
5 recover carbon dioxide having a sufficiently high pressure. Consequently, it is necessary to pressurize the recovered carbon dioxide again by means of a compressor.

(2) In the above-described process for the bulk removal of carbon dioxide, the natural gas from which carbon dioxide has been removed still contains about 1 to 5% of carbon dioxide.

SUMMARY OF THE INVENTION

The present invention has been made in view of the above-described existing state of the art, and it is an object thereof to provide a process for removing highly concentrated carbon dioxide from high-pressure natural gas and various
15 synthesis gases with the aid of a carbon dioxide absorbing fluid until a very low carbon dioxide concentration is reached and, moreover, for recovering high-pressure carbon dioxide from the absorbing fluid.

20 As a result of intensive investigations, the present inventors have found that carbon dioxide can be highly removed from a raw gas and, at the same time, carbon dioxide can be recovered in a high-pressure state, by treating the raw gas with an absorbing fluid so as to cause carbon dioxide
25 to be absorbed therein, heating the resulting carbon

dioxide-loaded absorbing fluid to liberate carbon dioxide in a high-pressure state and thereby regenerate the absorbing fluid partially, recycling a portion of the partially regenerated absorbing fluid to the absorption step, and
5 highly regenerating the remainder of the partially regenerated absorbing fluid and recycling the resulting highly regenerated absorbing fluid to the absorption step. The present invention has been completed on the basis of this finding.

10 That is, the present invention provides a process for the high removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas which comprises the steps of feeding a high-pressure raw gas containing 2 to 50% of carbon dioxide and having a pressure of not less than 2 kg/cm²
15 (absolute pressure) to a decarbonation tower consisting of a lower absorption section and an upper absorption section, where the raw gas is brought into gas-liquid contact with a partially regenerated absorbing fluid in the lower absorption section so as to cause carbon dioxide to be partially
20 absorbed thereinto, and then brought into gas-liquid contact with a regenerated absorbing fluid in the upper absorption section so as to cause carbon dioxide to be absorbed thereinto and removed until a very low carbon dioxide concentration is reached, and the refined gas having a carbon
25 dioxide concentration of 10 to 10,000 ppm is discharged out

of the system; heating the carbon dioxide-loaded absorbing fluid produced in the decarbonation tower and feeding it to a high-pressure regeneration tower where some carbon dioxide is liberated under a pressure ranging from 2 kg/cm² (absolute pressure) to the pressure of the raw gas to obtain a partially regenerated absorbing fluid, and a portion of the partially regenerated absorbing fluid is fed to the lower absorption section; feeding the remainder of the partially regenerated absorbing fluid to a low-pressure regeneration tower where carbon dioxide is liberated to obtain a regenerated absorbing fluid, and the regenerated absorbing fluid is fed to the upper absorption section; recovering high-pressure carbon dioxide by cooling the carbon dioxide liberated under pressure in the high-pressure regeneration tower and separating it from any entrained water; and recovering carbon dioxide by cooling the carbon dioxide liberated in the low-pressure regeneration tower and separating it from any entrained water, as well as a system therefor.

The present invention makes it possible to remove highly concentrated carbon dioxide from high-pressure natural gas and various synthesis gases until a very low carbon dioxide concentration of not greater than 1,000 ppm is reached and, moreover, to recover high-pressure carbon dioxide. As a result, the compression power required for subsequent use of

the carbon dioxide can be saved and the scale of the equipment can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram illustrating the process for the high removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas in accordance with the present invention; and

FIG. 2 is a flow diagram illustrating a conventional process for the high removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The raw gas treated according to the present invention is selected from natural gas and various synthesis gases which have a high pressure and contain carbon dioxide. Examples of such gases are carbon dioxide-containing gases which are obtained by the steam reforming or partial oxidation of naphtha, natural gas, heavy oil, coke or the like and have been subjected to a CO shift reaction for converting carbon monoxide to carbon dioxide. Preferably, these gases are used in the present invention after having been desulfurized to a sulfur compound concentration of not greater than 100 ppm.

Although no particular limitation is placed on the pressure of the raw gas, it is preferably not less than 2 kg/cm² and more preferably not less than 10 kg/cm². The upper limit of the pressure is not specifically defined, but

is usually in the range of 200 to 300 kg/cm². Similarly, although no particular limitation is placed on the carbon dioxide concentration of the raw gas, it is preferably in the range of 1 to 50% by volume and more preferably 10 to 30% by volume.

After being treated according to the present invention, the resulting purified gas has substantially the same pressure as the raw gas and a carbon dioxide concentration of 1 to 10,000 ppm and preferably 10 to 1,000 ppm.

The carbon dioxide absorbing fluid used in the present invention comprises an aqueous solution containing an absorbent selected from various basic compounds and mixtures thereof.

For this purpose, it is preferable to select an absorbing fluid having the following absorption capacity.

After having absorbed carbon dioxide by gas-liquid contact with a raw gas, the carbon dioxide absorbing fluid is partially regenerated in a high-pressure regeneration tower to liberate some of the carbon dioxide therefrom, and then recycled for use in the lower absorption step. Thus, its absorption capacity must be such that, when the partial pressure of carbon dioxide is 2 kg/cm² or greater, the difference in saturated carbon dioxide absorption level between the absorption temperature (e.g., 40°C) and the partial regeneration temperature (e.g., 120°C) is not less

than a specific value (e.g., not less than 30 Nm³ of CO₂ per m³ of the absorbing fluid and preferably not less than 40 Nm³ of CO₂ per m³ of the absorbing fluid).

Usually, if the temperature and the partial pressure of carbon dioxide are given, the saturated carbon dioxide absorption level of the aforesaid absorbing fluid shows a fixed value based on the saturated carbon dioxide absorption curve for that absorbing fluid, almost regardless of the type of the carbon dioxide-containing gas.

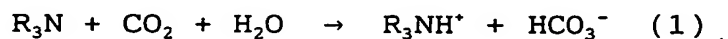
In the present invention, as shown in the Examples which will be given later, carbon dioxide is removed from high-pressure natural gas having a pressure of 30 kg/cm² or greater by absorbing it into a partially regenerated absorbing fluid, and the resulting loaded absorbing fluid is transferred to a partial regeneration step where, without being depressurized, it is heated to liberate carbon dioxide therefrom. Accordingly, it is preferable to use an absorbing fluid which can easily absorb carbon dioxide at a low temperature and a low partial pressure in the absorption step and can easily liberate carbon dioxide at a high temperature and a high partial pressure in the regeneration step.

Consequently, a physical absorbing fluid or an absorbing fluid comprising amine having strong physical absorption properties is preferably used as the aforesaid carbon dioxide absorbing fluid.

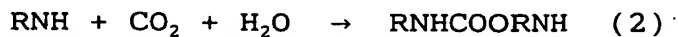
The physical absorbing fluid includes methanol and polyethylene glycol dimethyl ether.

As for the amine having strong physical absorption properties, specifically, amines, amino acids and alkali metal salts of the amino acids are used. If necessary, amines having strong chemical absorption properties, alkali metal carbonates and the like may be added thereto.

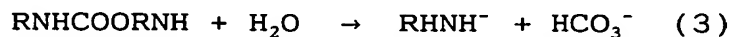
Typical examples of the amines having strong physical absorption properties are tertiary amines, which mainly react below.



Hence, the tertiary amines may be easily regenerated by flash or the like. On the other hand, primary amines and secondary amines are bases having strong chemical absorption properties and mainly react below.



The regeneration requires heat of decomposition. Even in the case of the equation (2), however, the amines with high steric hindrance tend to form a bond having closer characteristic to an ionic bond than a chemical bond, resulting the further reaction below.



Accordingly, the amines having strong physical absorption properties include not only tertiary amines but also primary amines and secondary amines.

Hence, preferred examples of the amines are hindered amines. The preferred hindered amines include N-methyldiethanolamine (MDEA), triethanolamine (TEA), dimethylamino-1,3-propanediol (DMAPD) and diethylamino-1,3-propanediol (DEAPD).

Useful alkali metal salts include potassium carbonate.

Moreover, carbon dioxide absorption promoters such as piperazine, substituted piperazines, piperidine and substituted piperidines may be added to the above-described carbon dioxide absorbing fluid.

The carbon dioxide absorbing fluid may be a 20-80% aqueous solution of the absorbent, though the concentration depends on the type of the absorbent and the conditions of use.

If necessary, a solvent such as N-methylpyrrolidone or sulfolane may be added to the carbon dioxide absorbing fluid.

The high-pressure carbon dioxide recovered from the carbon dioxide absorbing fluid has a pressure of not less than 2 kg/cm² and preferably a pressure ranging from 10 kg/cm² to a value almost equal to the pressure of the raw gas, though the pressure depends on the type of the raw gas and the use of carbon dioxide.

Accordingly, the high-pressure regeneration tower is operated at the aforesaid pressure, and the loaded absorbing fluid is heated to a temperature of 90 to 150°C and preferably 100 to 140°C. Thus, water and carbon dioxide are

partially liberated from the loaded absorbing fluid, whereby the loaded absorbing fluid is partially regenerated.

The partially regenerated absorbing fluid is more highly regenerated under conditions including an operating pressure of not greater than 2 kg/cm² and preferably 0.5 to 1 kg/cm² and a fluid temperature of 100 to 150°C and preferably 110 to 140°C, for example, by circulating it through a reboiler and heating it therewith.

The degree of regeneration of the partially regenerated absorbing fluid fed to the lower absorption section of the decarbonation tower, the degree of regeneration of the regenerated absorbing fluid fed to the upper absorption section thereof, and the feed ratio of them depend on the type of the absorbing fluid, the carbon dioxide concentration, pressure and other conditions of the raw gas, the carbon dioxide concentration of the refined gas, and the flow rate, concentration, pressure and other conditions of the recovered high-pressure carbon dioxide. For example, the degree of partial regeneration is in the range of 0.05 to 0.3 mole of CO₂ per mole of the absorbing fluid, the degree of regeneration is in the range of about 0.01 to 0.1 mole of CO₂ per mole of the absorbing fluid, and the proportion of the partially regenerated absorbing fluid fed to the decarbonation tower is in the range of 30 to 95%.

The process of the present invention is specifically

described below with reference to FIG. 1.

A raw gas 1 is fed to the bottom of a decarbonation tower 2. In a lower absorption section 3, raw gas 1 comes into gas-liquid contact with a partially regenerated absorbing fluid 21, so that carbon dioxide is partially absorbed thereinto. Then, in an upper absorption section 4, raw gas 1 comes into gas-liquid contact with a regenerated absorbing fluid 22, so that carbon dioxide is further absorbed until a very low carbon dioxide concentration is reached. The resulting gas is discharged out of the system as a refined gas 17.

In the above-described process, regenerated absorbing fluid 22 flows down through upper absorption section 4 while coming into gas-liquid contact with raw gas 1, and mixes with partially regenerated absorbing fluid 21 in lower absorption section 3. The resulting absorbing fluid flows down through lower absorption section 3 while coming into gas-liquid contact with raw gas 1, and is withdrawn from the bottom of decarbonation tower 2.

The carbon dioxide-loaded absorbing fluid 20 emerging from the bottom of decarbonation tower 2 is heated, if necessary, by heat exchange with partially regenerated absorbing fluid 21 or regenerated absorbing fluid 22 in a heat exchanger 5 or 6, further heated to a predetermined temperature by means of a heater 7, and then fed to a high-temperature regeneration

tower 8.

The resulting partially regenerated absorbing fluid 21 is withdrawn from the bottom of high-temperature regeneration tower 8. A portion thereof is cooled in heat exchanger 5, further cooled in heat exchanger 15 if necessary, and then fed to lower absorption section 3.

The mixture of water and carbon dioxide discharged from the top of high-pressure regeneration tower 8 is cooled in a condenser 9 and introduced into a gas-liquid separator 10 where it is separated into water and high-pressure carbon dioxide 18. The water is recycled to the top of high-pressure regeneration tower 8. If necessary, some of the water may be fed to the top of absorption tower 2, or used for recovery of the absorbing fluid or as recycle water to a low-pressure regeneration tower.

The remainder of partially regenerated absorbing fluid 21 is fed to a low-pressure regeneration tower 11 which is operated at an absolute pressure of less than 2 kg/cm² or at reduced pressure and equipped with a reboiler 12 to heat the bottom fluid. Thus, water and carbon dioxide are liberated from the partially regenerated absorbing fluid, so that it is highly regenerated. The degree of regeneration of the loaded absorbing fluid is determined by the heating temperature, residence time and operating pressure employed for the treatment of the loaded absorbing fluid in low-pressure

regeneration tower 11.

The regenerated absorbing fluid 22 is withdrawn from the bottom of low-pressure regeneration tower 11. A portion thereof is cooled in heat exchanger 6, further cooled in heat exchanger 16 as required, and then fed to upper absorption section 4.

The mixture of water and carbon dioxide discharged from the top of low-pressure regeneration tower 11 is cooled in a condenser 13 and introduced into a gas-liquid separator 14 where it is separated into water and low-pressure carbon dioxide 19. The water is recycled to the top of low-pressure regeneration tower 11. If necessary, some of the water may be fed to the top of absorption tower 2, or used for recovery of the absorbing fluid or as recycle water to the high-pressure regeneration tower.

The absorption tower and the several regeneration towers may comprise plate towers or packed towers, provided that they can bring about efficient gas-liquid contact and cause a small pressure loss. To this end, there may be used any of various conventional packing materials such as those of the wetted-wall type.

Greater economy is achieved as the proportion of high-pressure carbon dioxide recovered according to the present invention becomes higher. In the present invention, not less than 50%, preferably not less than 70%, and most preferably

not less than 90% of carbon dioxide can be recovered at high pressure.

Thus, the present invention makes it possible to recover carbon dioxide at high pressure, resulting in a great saving of compression power and a reduction in the scale of the equipment.

The present invention is further illustrated by the following examples. However, these examples are not to be construed to limit the scope of the invention.

Example 1

This example relates to an application of the process illustrated in the flow diagram of FIG. 1 in which a raw gas for use in ammonia synthesis obtained by the reforming of natural gas was treated with an absorbing fluid comprising an aqueous solution containing 45% by weight of MDEA and 4% by weight of piperazine to remove carbon dioxide therefrom.

A raw gas comprising hydrogen, nitrogen, hydrocarbons and 19% by volume of carbon dioxide was fed to the lower part of an absorption tower under conditions including a pressure of 34 kgG/cm², a temperature of 45°C and a flow rate of 292,000 Nm³/hr.

In a lower absorption section of the absorption tower, the ascending raw gas came into gas-liquid contact with 1,716 m³/hr of a partially regenerated absorbing fluid. Thus, in the lower absorption section, carbon dioxide was partially

removed from the raw gas until its carbon dioxide concentration was reduced to about 2% by volume. Moreover, the raw gas came into gas-liquid contact with 163 m³/hr of a regenerated absorbing fluid in an upper absorption section.

5 The refined raw gas, which had a carbon dioxide concentration of 490 ppm, a temperature of 39°C and a pressure of 33 kgG/cm², was discharged from the top of the absorption tower.

The loaded absorbing fluid having carbon dioxide absorbed thereinto had a fluid temperature of 55°C and contained about 78 Nm³ of carbon dioxide (CO₂) per m³ of the absorbing fluid. This loaded absorbing fluid was subjected to heat exchange, then heated to 120°C, and fed to a high-pressure regeneration tower where it was partially regenerated. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were cooled in a condenser and introduced into a gas-liquid separator where carbon dioxide was separated. The cooled and separated carbon dioxide had a temperature of about 40°C, a pressure of 10 kgG/cm² and a flow rate of 49,800 Nm³/hr. This carbon dioxide was 20 pressurized to 190 kgG/cm² by means of a compressor (not shown) and used for the synthesis of urea.

On the other hand, the partially regenerated absorbing fluid withdrawn from the bottom of the high-pressure regeneration tower had a temperature of 100°C and contained 25 about 43 Nm³ of carbon dioxide (CO₂) per m³ of the absorbing

fluid. A portion of this partially regenerated absorbing fluid was subjected to heat exchange with the loaded absorbing fluid, further cooled to 38°C, and fed to the lower absorption section of the absorption tower.

5 The remainder (163 m³/hr) of the partially regenerated absorbing fluid was fed to a low-pressure regeneration tower where it was depressurized to 0.85 kgG/cm² and regenerated with carbon dioxide and water discharged from the top of the tower. The bottom fluid was heated to about 110°C by means
10 of a reboiler provided at the bottom of the low-pressure regeneration tower, and recycled to the low-pressure regeneration tower. Thus, there was obtained a regenerated absorbing fluid containing 1.2 Nm³ of carbon dioxide (CO₂) per m³ of the absorbing fluid. The liberated carbon dioxide
15 and water, together with a small amount of the absorbing fluid, were cooled in a condenser and introduced into a gas-liquid separator where carbon dioxide was separated. The cooled and separated carbon dioxide had a temperature of about 40°C, a pressure of 0.35 kgG/cm² and a flow rate of
20 5,700 Nm³/hr.

The regenerated absorbing fluid withdrawn from the bottom of the low-pressure regeneration tower had a temperature of about 110°C and was fed to the upper absorption section of the absorption tower. During this course, the regenerated
25 absorbing fluid having a temperature of 110°C was subjected

to heat exchange with the loaded absorbing fluid having a lower temperature, and further cooled to 38°C.

Of all the carbon dioxide recovered in the above-described manner, 90% was recovered in the high-pressure regeneration tower and 10% was recovered in the low-pressure regeneration tower.

Thus, the carbon dioxide concentration of the raw gas for use in ammonia synthesis was reduced to a level sufficient for supply to an ammonia synthesis process. Moreover, the pressure of the recovered carbon dioxide was so high that the compression power required for the synthesis of urea could be saved and the scale of the equipment could be reduced.

Example 2

This example relates to an application of the process illustrated in FIG. 1 in which a raw gas for use in ammonia synthesis obtained by the reforming of natural gas was treated with an absorbing fluid comprising an aqueous solution containing 45% by weight of MDEA and 4% by weight of piperazine to remove carbon dioxide therefrom.

A raw gas 1 comprising hydrogen, nitrogen, hydrocarbons and 19% by volume of carbon dioxide was fed to the lower part of an absorption tower 2 under conditions including a pressure of 34 kgG/cm², a temperature of 45°C and a flow rate of 292,000 Nm³/hr.

In a lower absorption section 3 of absorption tower 2, the

ascending raw gas 1 came into gas-liquid contact with a partially regenerated absorbing fluid 21 ($1,716 \text{ m}^3/\text{hr}$). Thus, in lower absorption section 3, carbon dioxide was partially removed from raw gas 1 until its carbon dioxide concentration was reduced to about 2% by volume. Moreover, raw gas 1 came into gas-liquid contact with a regenerated absorbing fluid 22 ($200 \text{ m}^3/\text{hr}$) in an upper absorption section 4. The refined gas, which had a carbon dioxide concentration of 50 ppm, a temperature of 39°C and a pressure of 33 kgG/cm^2 , was discharged from the top of absorption tower 2.

The loaded absorbing fluid 20 having carbon dioxide absorbed thereinto contained about 78 Nm^3 of carbon dioxide (CO_2) per m^3 of the absorbing fluid. This loaded absorbing fluid 20 was subjected to heat exchange, then heated to 120°C , and fed to a high-pressure regeneration tower 8 where it was partially regenerated. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were cooled in a condenser 9 and introduced into a gas-liquid separator 10 where carbon dioxide 18 was separated. The cooled and separated carbon dioxide 18 had a temperature of about 40°C , a pressure of 33 kgG/cm^2 and a flow rate of $49,640 \text{ Nm}^3/\text{hr}$. This carbon dioxide 18 was pressurized to 150 kgG/cm^2 by means of a compressor (not shown) and used for the synthesis of urea.

On the other hand, the partially regenerated absorbing

fluid 21 withdrawn from the bottom of high-pressure regeneration tower 8 had a temperature of 100°C and contained 29.2 Nm³ of carbon dioxide (CO₂) per m³ of the absorbing fluid. A portion of this partially regenerated absorbing fluid 21 was subjected to heat exchange with loaded absorbing fluid 20, further cooled to 38°C, and fed to lower absorption section 3 of absorption tower 2.

The remainder (200 m³/hr) of partially regenerated absorbing fluid 21 was fed to a low-pressure regeneration tower 11 where it was depressurized to 0.85 kgG/cm² and regenerated with carbon dioxide and water discharged from the top of the tower. The bottom fluid was heated to about 110°C by means of a reboiler 12 provided at the lower part of low-pressure regeneration tower 11, and recycled to low-pressure regeneration tower 11. Thus, there was obtained a regenerated absorbing fluid 22 containing 5 Nm³ of carbon dioxide (CO₂) per m³ of the absorbing fluid. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were cooled in a condenser 13 and introduced into a gas-liquid separator 14 where carbon dioxide 19 was separated. The cooled and separated carbon dioxide 19 had a temperature of about 40°C, a pressure of 0.35 kgG/cm² and a flow rate of 5,500 Nm³/hr.

The regenerated absorbing fluid 22 withdrawn from the bottom of low-pressure regeneration tower 11 had a

temperature of about 110°C and was fed to upper absorption section 4 of absorption tower 2. During this course, regenerated absorbing fluid 22 having a temperature of 110°C was subjected to heat exchange with loaded absorbing fluid 20 having a lower temperature, and further cooled to 38°C.

Of all the carbon dioxide recovered in the above-described manner, 90% was recovered in high-pressure regeneration tower 8 and 10% was recovered in low-pressure regeneration tower 11.

Thus, the carbon dioxide concentration of the raw gas for use in ammonia synthesis was reduced to a level sufficient for supply to an ammonia synthesis process. Moreover, the pressure of the recovered carbon dioxide was so high that the compression power required for the synthesis of urea could be saved and the scale of the equipment could be reduced.

Example 3

This example relates to an application of the process illustrated in the flow diagram of FIG. 1 in which natural gas was treated with an absorbing fluid comprising an aqueous solution containing 45% by weight of MDEA to remove carbon dioxide therefrom.

Natural gas 1 having a carbon dioxide concentration of 26% by volume was fed to the lower part of an absorption tower 2 under conditions including a pressure of 58 kgG/cm² and a temperature of 25°C.

A lower absorption section 3 of absorption tower 2 was packed, for example, with a wetted-wall type packing material, so that the ascending natural gas 1 came into efficient gas-liquid contact with a partially regenerated absorbing fluid 21. Thus, in lower absorption section 3, carbon dioxide was partially removed from natural gas 1 until its carbon dioxide concentration was reduced to about 3% by volume. Moreover, the ascending natural gas 1 came into efficient gas-liquid contact with a regenerated absorbing fluid 22 in an upper absorption section 4 comprising a similar wetted-wall type packed bed. The refined gas 17 was discharged from the top of absorption tower 2. This refined gas 17 had a carbon dioxide concentration of 50 ppm, a temperature of 50°C and a pressure of 58 kgG/cm².

The loaded absorbing fluid 20 having carbon dioxide absorbed therein was subjected to heat exchange, then heated to 130°C, and fed to a high-pressure regeneration tower 8 where it was partially regenerated.

In high-pressure regeneration tower 8, the carbon dioxide liberated by the aforesaid heating was separated from absorbing fluid 20 to obtain a partially regenerated absorbing fluid 21. Accordingly, the use of a heater such as a reboiler 12 is unnecessary, but such a heater may be used as required. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were

cooled in a condenser 9 and introduced into a gas-liquid separator 10 where carbon dioxide 18 was separated. The cooled and separated carbon dioxide 18 had a temperature of about 40°C and a pressure of 55 kgG/cm² which was almost equal to the pressure of natural gas 1 used as the raw gas. This carbon dioxide 18 may be pressurized to 150 kgG/cm² by means of a compressor (not shown) and used for the purpose of tertiary oil recovery or storage in the earth.

On the other hand, the partially regenerated absorbing fluid 21 withdrawn from the bottom of high-pressure regeneration tower 8 had a temperature of about 130°C, and a predetermined portion thereof was fed to lower absorption section 3 of absorption tower 2. During this course, partially regenerated absorbing fluid 21 was subjected to heat exchange with loaded absorbing fluid 20 having a lower temperature, and further cooled to a required temperature.

The remainder of partially regenerated absorbing fluid 21 was fed to a low-pressure regeneration tower 11 where it was depressurized to 0.85 kgG/cm² and regenerated with carbon dioxide 19 and water discharged from the top of the tower. The bottom fluid was heated to about 130°C by means of a reboiler 12 provided at the lower part of low-pressure regeneration tower 11, and recycled to low-pressure regeneration tower 11. Thus, there was obtained a regenerated absorbing fluid 22 containing about 45% by weight

of MDEA. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were cooled in a condenser 13 and introduced into a gas-liquid separator 14 where carbon dioxide 19 was separated. The cooled and
5 separated carbon dioxide 19 had a temperature of about 40°C and a pressure of 0.35 kgG/cm², and was used as an industrial gas.

The regenerated absorbing fluid 22 withdrawn from the bottom of low-pressure regeneration tower 11 had a
10 temperature of about 130°C and was fed to upper absorption section 4 of absorption tower 2. During this course, regenerated absorbing fluid 22 having a temperature of 130°C was subjected to heat exchange with loaded absorbing fluid 20 having a lower temperature, and further cooled to a required
15 temperature.

Of all the carbon dioxide recovered in the above-described manner, 85% was recovered in high-pressure regeneration tower 8 and 15% was recovered in low-pressure regeneration tower
11.

20 Thus, the carbon dioxide concentration of the refined natural gas 17 was reduced to a level which would not cause solid dry ice to be produced during the manufacture of LNG. Moreover, the pressure of the recovered carbon dioxide was so high that the compression power required for the production
25 of liquid carbon dioxide for use in tertiary oil recovery

could be saved and the scale of the equipment could be reduced.

Example 4

5 This example relates to an application of the process illustrated in the flow diagram of FIG. 1 in which raw hydrogen gas for use in chemical syntheses obtained by the reforming of natural gas was treated with an absorbing fluid comprising an aqueous solution containing 40% by weight of triethanolamine (TEA) and 4% by weight of piperazine as a reaction accelerator to remove carbon dioxide therefrom.

10 A raw gas 1 comprising 68 mole % of hydrogen, 12 mole % of methane, 19 mole % of carbon dioxide, and other inert gases was fed to the lower part of an absorption tower 2 under conditions including a pressure of 33 kgG/cm² and a temperature of 60°C.

15 In a lower absorption section 3 of absorption tower 2, the ascending raw gas 1 came into gas-liquid contact with a partially regenerated absorbing fluid 21. Thus, in lower absorption section 3, carbon dioxide was partially removed from raw gas 1 until its carbon dioxide concentration was reduced to about 1% by volume. Moreover, the ascending raw gas 1 came into gas-liquid contact with a regenerated absorbing fluid 22 in an upper absorption section 4. The refined gas 17, which had a carbon dioxide concentration of 200 ppm, a temperature of 40°C and a pressure of 32 kgG/cm²,

20

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was discharged from the top of absorption tower 2.

5 The loaded absorbing fluid 20 having carbon dioxide absorbed thereinto was subjected to heat exchange, then heated to 120°C, and fed to a high-pressure regeneration tower 8 where about 60% of the carbon dioxide present in loaded absorbing fluid 20 was liberated. The liberated carbon dioxide and water, together with a small amount of the absorbing fluid, were cooled in a condenser 9 and introduced into a gas-liquid separator 10 where carbon dioxide 18 was separated. The cooled and separated carbon dioxide 18 had a temperature of about 40°C and a pressure of 9 kgG/cm². This carbon dioxide 18 was pressurized to 100 kgG/cm² by means of a compressor (not shown) and used for the production of liquid carbon dioxide.

15 On the other hand, the partially regenerated absorbing fluid 21 withdrawn from the bottom of high-pressure regeneration tower 8 was subjected to heat exchange with loaded absorbing fluid 20, further cooled, and fed to lower absorption section 3 of absorption tower 2.

20 The remainder (about 10%) of partially regenerated absorbing fluid 21 was fed to a low-pressure regeneration tower 11 where it was depressurized to 0.85 kgG/cm² and regenerated with carbon dioxide 19 and water discharged from the top of the tower. The bottom fluid was heated to about 25 130°C by means of a reboiler 12 provided at the lower part of

low-pressure regeneration tower 11, and recycled to low-pressure regeneration tower 11. From the resulting regenerated absorbing fluid 22, about 98% of the carbon dioxide present in the starting loaded absorbing fluid 20 had been liberated. The carbon dioxide 19 separated by means of a gas-liquid separator 14 had a temperature of about 40°C and a pressure of 0.35 kgG/cm². This carbon dioxide 19 was also pressurized to 100 kgG/cm² by means of a compressor and used for the production of liquid carbon dioxide.

The regenerated absorbing fluid 22 withdrawn from the bottom of low-pressure regeneration tower 11 had a temperature of about 130°C and was fed to upper absorption section 4 of absorption tower 2. During this course, regenerated absorbing fluid 22 was subjected to heat exchange with loaded absorbing fluid 20 having a lower temperature, and further cooled with cooling water.

Of all the carbon dioxide recovered in the above-described manner, 92% was recovered in high-pressure regeneration tower 8 and 8% was recovered in low-pressure regeneration tower 11.

Thus, the carbon dioxide concentration of the raw hydrogen gas for use in chemical syntheses was reduced to a level sufficient for supply to subsequent process steps. Moreover, the proportion of the recovered high-pressure carbon dioxide was so high that the compression power required for the production of liquid carbon dioxide could be saved and the

scale of the equipment could be reduced.

Comparative Example 1

Using the same high-pressure natural gas and absorbing fluid as used in Example 3, the natural gas was treated in a conventional process (see FIG. 2) in order to reduce its carbon dioxide concentration to 50 ppm and, moreover, recover carbon dioxide.

The carbon dioxide-loaded absorbing fluid 120 was fed to a first flash drum 123 where it was flashed under a pressure of 3.8 kgG/cm² to liberate a portion of the carbon dioxide present in loaded absorbing fluid 120 and thereby obtain a partially regenerated absorbing fluid. This partially regenerated absorbing fluid is further heated in a heater 107 and fed to a second flash drum 124 where it was flashed again to obtain a regenerated absorbing fluid 122.

The carbon dioxide obtained in first flash drum 123 had a pressure of 3.8 kgG/cm², which was far lower than the pressure (55 kgG/cm²) of the carbon dioxide obtained in Example 1. Accordingly, in order to produce liquid carbon dioxide for use in tertiary oil recovery, the process of Comparative Example 1 was more disadvantageous than the process of Example 1 from the viewpoint of compression power and equipment. In this process, natural gas 101 is fed to absorption tower 102 and discharged as a refined gas 117.

Numerical 109 designates an overhead condenser disposed between

The claims defining the invention are as follows:-

1. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas which comprises the steps of feeding a high-pressure raw gas
5 containing carbon dioxide to a decarbonation tower having a lower absorption section and an upper absorption section, where the raw gas is brought into gas-liquid contact with a partially regenerated absorbing fluid in the lower absorption section so as to cause carbon dioxide to be partially
10 absorbed thereinto, and then brought into gas-liquid contact with a regenerated absorbing fluid in the upper absorption section so as to cause carbon dioxide to be absorbed thereinto until a very low carbon dioxide concentration is reached, and the carbon dioxide-free refined gas is
15 discharged out of the system; heating the carbon dioxide-loaded absorbing fluid produced in the decarbonation tower and feeding it to a high-pressure regeneration tower where some carbon dioxide is liberated under pressure to obtain a partially regenerated absorbing fluid, and a portion of the
20 partially regenerated absorbing fluid is fed to the lower absorption section; feeding the remainder of the partially regenerated absorbing fluid to a low-pressure regeneration tower where carbon dioxide is liberated to obtain a regenerated absorbing fluid, and the regenerated absorbing
25 fluid is fed to the upper absorption section; recovering

high-pressure carbon dioxide by cooling the carbon dioxide liberated under pressure in the high-pressure regeneration tower and separating it from any entrained water; and recovering carbon dioxide by cooling the carbon dioxide liberated in the low-pressure regeneration tower and separating it from any entrained water.

2. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to claim 1 wherein the high-pressure raw gas has a carbon dioxide concentration of 2 to 50%.

3. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to claim 1 or 2 wherein the high-pressure raw gas has a pressure of not less than 2 kg/cm² (absolute pressure).

4. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to any one of claims 1-3 wherein the refined gas has a carbon dioxide concentration of 10 to 10,000 ppm.

5. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to any one of claims 1-4 wherein the heating temperature of the carbon dioxide-loaded absorbing fluid at which some carbon dioxide is liberated from the carbon dioxide-loaded absorbing fluid to obtain a partially regenerated absorbing fluid is in the range of 90 to 150°C.

6. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to any one of claims 1-5 wherein the pressure under which some carbon dioxide is liberated from the carbon dioxide-loaded absorbing fluid to obtain a partially regenerated absorbing fluid ranges from 2 kg/cm² (absolute pressure) to the pressure of the raw gas.

7. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to any one of claims 1-6 wherein the heating temperature of the partially regenerated absorbing fluid at which carbon dioxide is liberated from the remainder of the partially regenerated absorbing fluid to obtain a regenerated absorbing fluid is in the range of 100 to 150°C.

8. A process for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas according to any one of claims 1-7 wherein the pressure under which carbon dioxide is liberated from the remainder of the partially regenerated absorbing fluid to obtain a regenerated absorbing fluid is less than 2 kg/cm² (absolute pressure).

9. A system for the removal and high-pressure recovery of carbon dioxide from a high-pressure raw gas which comprises a decarbonation tower having a lower absorption section and an upper absorption section, a heater for a carbon dioxide-loaded absorbing fluid, a high-pressure regeneration tower

for the carbon dioxide-loaded absorbing fluid, a cooler and a gas-liquid separator provided at the top of the high-pressure regeneration tower, a low-pressure regeneration tower for a partially regenerated absorbing fluid, a heater provided at the bottom of the low-pressure regeneration tower, and a cooler and a gas-liquid separator provided at the top of the low-pressure regeneration tower, whereby a high-pressure raw gas containing carbon dioxide is fed to the decarbonation tower where the raw gas is brought into gas-liquid contact with the partially regenerated absorbing fluid in the lower absorption section so as to cause carbon dioxide to be partially absorbed thereinto, and then brought into gas-liquid contact with the regenerated absorbing fluid in the upper absorption section so as to cause carbon dioxide to be absorbed thereinto until a very low carbon dioxide concentration is reached, and the carbon dioxide-free refined gas is discharged out of the system; the carbon dioxide-loaded absorbing fluid produced in the decarbonation tower is heated and fed to the high-pressure regeneration tower where some carbon dioxide is liberated under pressure to obtain a partially regenerated absorbing fluid, and a portion of the partially regenerated absorbing fluid is fed to the lower absorption section; the remainder of the partially regenerated absorbing fluid is fed to a low-pressure regeneration tower where carbon dioxide is liberated to

obtain a regenerated absorbing fluid, and the regenerated absorbing fluid is fed to the upper absorption section; high-pressure carbon dioxide is recovered by cooling the carbon dioxide liberated under pressure in the high-pressure regeneration tower and separating it from any entrained water by means of the cooler and gas-liquid separator provided at the top of the high-pressure regeneration tower; and carbon dioxide is recovered by cooling the carbon dioxide liberated in the low-pressure regeneration tower and separating it from any entrained water by means of the cooler and gas-liquid separator provided at the top of the low-pressure regeneration tower.

10. A process for the removal and high-pressure recoveries of carbon dioxide from a high-pressure raw gas substantially as hereinbefore described in any one of Examples 1 to 4.

11. A system for the removal and high-pressure recoveries of carbon dioxide from a high-pressure raw gas substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

DATED THIS 10TH DAY OF JULY 1997

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FIG. 1

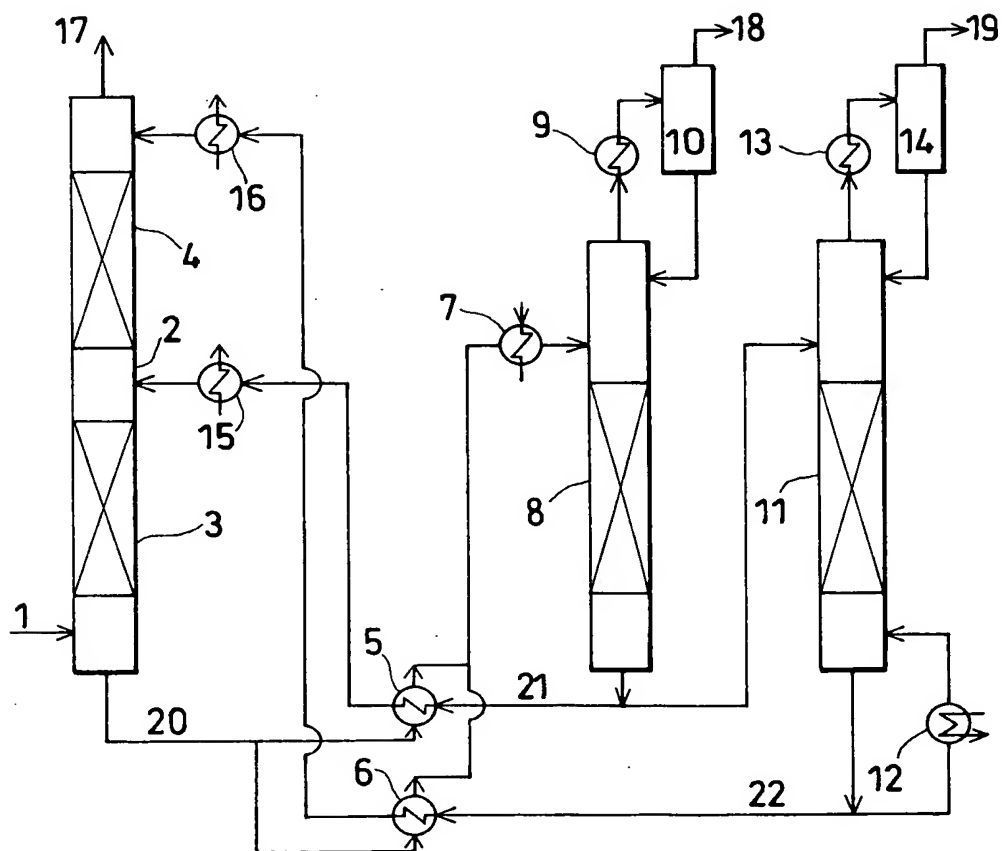


FIG. 2

